formulation Kanemite® in Japan and in some other countries where the problems of resistant mites have become pronounced. It is clear that the quinone metabolite DHN is the active moiety, that it is produced metabolically in mite cells and, because it acts at Complex III stage, that it can be used to control mite populations which are resistant to other miticides.

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Verbena × *hybrida* flower volatiles attractive to Western flower thrips, *Frankliniella occidentalis*

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Abstract: Western flower thrips (WFT) are attracted to three flowering verbena cultivars. The volatile components of these cultivars contain different enantiomers of linalool oxide which have been synthesised and one shown to be attractive to WFT.

Keywords: Western flower thrips; *Frankliniella occidentalis*; *Verbena* × *hybrida*; linalool oxide; enantioselective synthesis

Integrated pest management strategies involving the use of predators are commonly used for control of the Western flower thrips (WFT), *Franklinella occidentalis* Perg, in glasshouses. In agricultural studies, trap crops have shown potential as part of a 'push pull' strategy to concentrate pest insects in particular areas where control agents can be applied. The use of such a strategy under glass would reduce application times and costs of biocontrol agents against pest insects. In glasshouse trials, flowering *Verbena* × *hybrida* Voss plants attracted WFT from ivy geraniums and chrysanthemums and are therefore potential trap plants. Furthermore, the flower volatiles isolated from Sissinghurst Pink, Tapien Pink and Pink Parfait verbena cultivars were particularly attractive to WFT in olfactometer tests. The volatiles identified have potential for increasing the attractiveness of verbena trap plants or attracting thrips to sticky traps at times when verbena plants are not available.

Volatiles from the three cultivars were collected by air entrainment and the major components characterised by GC-MS and GC coinjection with authentic standards (Table 1). The major components of Tapien Pink and Pink Parfait were shown to be different isomers of linalool oxide, both of which were present in Sissinghurst Pink. Elucidation of the structure of the major Tapien Pink and Pink Parfait volatiles was achieved by microcell [^{1}H]NMR spectroscopy, which revealed that the Tapien Pink volatile (400 µg) and the Pink Parfait volatile (40 µg) were diastereoisomers of linalool oxide pyran. Other components identified in both volatiles were an oxidised linalool oxide isomer, a tetraene and a nonatriene, all of which were synthesised for stereochemical assignment. Synthesis of all four enantiomerically pure isomers of the linalool oxide pyrans was performed as shown (Fig 1). The *N*-phenyl carbamate group is electron-withdrawing and so dihydroxylation of **1** with AD-mix β at <5 °C was regioselective for the more reactive alkene. [AD-mix-α and AD-mix-β are asymmetric dehydroxylation reagents (supplied by Aldrich Chemical Co) which are enantioselective.] Protection of the secondary alcohol of **2** by acetylation was followed by cyclisation and deprotection to generate the two diastereoisomers **3** and **4** which were separated by chromatography.[1] The other two enantiomerically pure diastereoisomers of linalool oxide pyran, **5** and **6**, were synthesised in the

Table 1. Relative proportions of volatile components from air entrainment over flowers of three cultivars of verbena, estimated by GC trace integration as a percentage of the total

Compound	*Sissinghurst Pink (%)*	*Pink Parfait (%)*	*Tapien Pink (%)*
Benzaldehyde	–	–	1.0
Methyl benzoate	–	2.1	–
(*E*)-β-Ocimene	14.4	–	–
(*S*)-Linalool	trace	1.8	11.5
(6*S*)-Pyranone **9**	5.3	5.4	–
(3*E*)-4,8-Dimethyl-1,3,7-nonatriene	5.6	16.7	–
(3*R*,6*S*)-Pyranol **3**	9	1.4	86
(3*S*,6*S*)-Pyranol **5**	7.6	61.3	–
Pentadecane	33.6	–	–
(3*E*,7*E*)-4,8,12-Trimethyl-1,3,7,11-tridecatetraene	1.0	5.1	–

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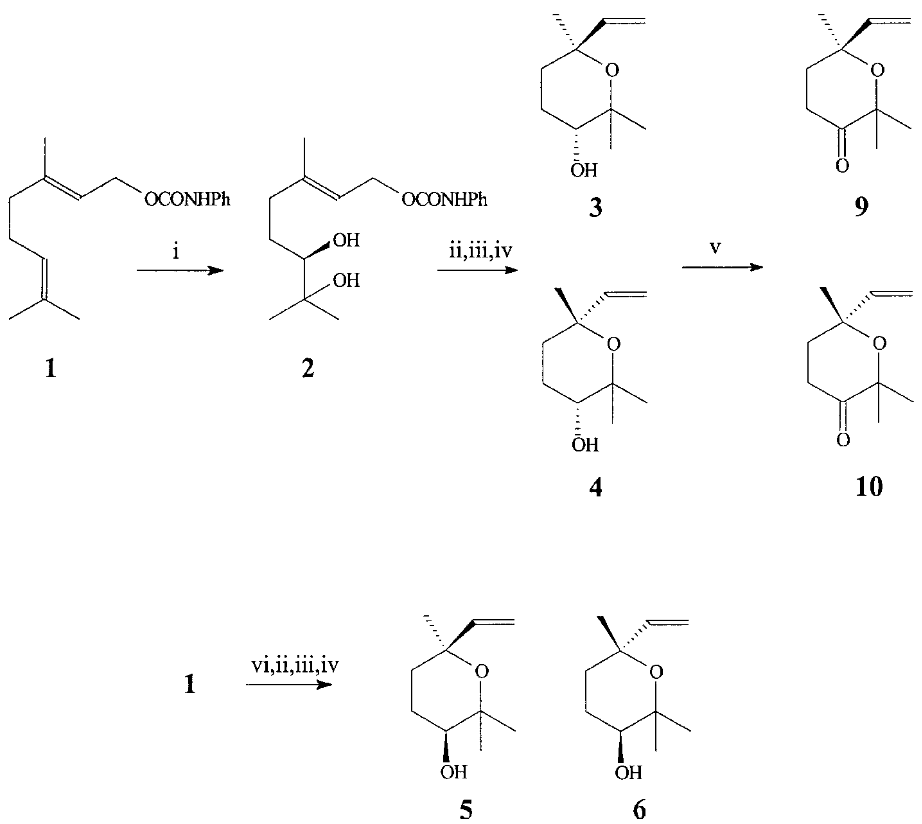

Figure 1. Synthesis of four enantiomers of the linalool oxide pyrans and their oxidation product. (i) AD-mix-β, (ii) acetic anhydride/pyridine, (iii) $SnCl_4$, (iv) $LiAlH_4$, (v) Jones' reagent, (vi) AD-mix-α.

same way but using AD-mix-α. Stereochemical assignment of the diastereoisomers was achieved chemically by converting the vinyl groups to the carboxylic acids by ruthenium chloride/sodium periodate oxidation (Fig 2). The diastereoisomer having the *cisoid* hydroxyl and carboxyl group can intramolecularly cyclise to lactone **8**, while **7** remains a hydroxy acid. Coinjection using chiral GC (β-cyclodextrin, 0.25 mm ID × 30 m, 40 °C to 180 °C at 3 °C min^{-1}) revealed the major Tapien Pink component to be (3*R*,6*S*)-tetrahydro-2,2,6-trimethyl-6-vinyl-2*H*-pyran-3-ol (**3**) and the Pink Parfait component to be (3*S*,6*S*)-tetrahydro-2,2,6-trimethyl-6-vinyl-2*H*-pyran-3-ol (**5**). Sissinghurst Pink produces both **3** and **5**. Jones' oxidation

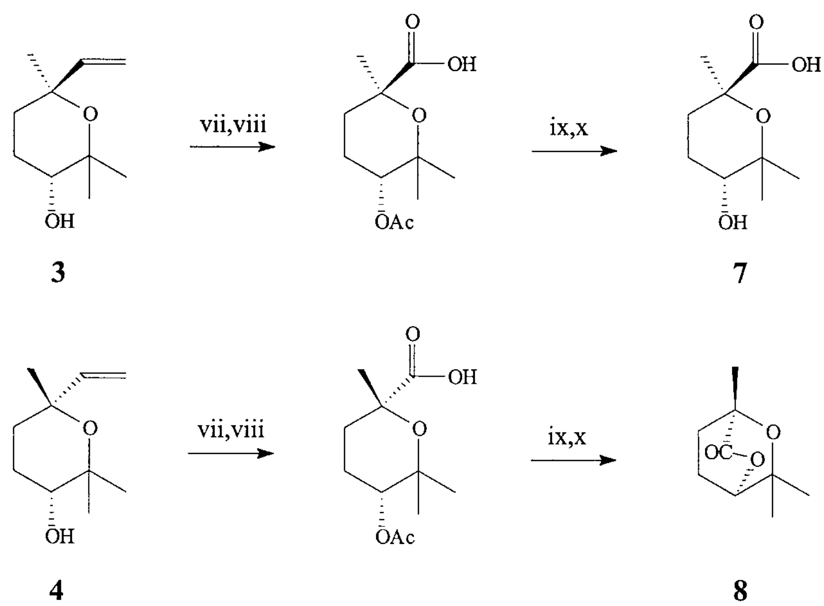

Figure 2. Stereochemical assignment of the diastereoisomers **3** and **4**. (vii) Acetyl chloride/pyridine, (viii) $RuCl_3.H_2O/NaIO_4$, (ix) KOH, (x) HCl.

of the pyranols **3** and **4** generated (6*S*)- and (6*R*)-tetrahydro-2,2,6-trimethyl-6-vinyl-2*H*-pyran-3-ones **9** and **10** respectively. Coinjection by chiral GC showed (6*S*)-tetrahydro-2,2,6-trimethyl-6-vinyl-2*H*-pyran-3-one **9** to be identical to the component produced by Sissinghurst Pink and Pink Parfait. In olfactometer studies, WFT were attracted to **5** but not to **3** or to a mixture of **5** and **3** in the ratio produced by Sissinghurst Pink cultivar, suggesting that there may be separate olfactory receptors for the two diastereoisomers of linalool oxide and that other components of the flower volatiles must contribute to the attractiveness of the odours from Tapien Pink and Pink Parfait.

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Developing new herbicide models from allelochemicals†

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Abstract: Plants contain allelochemicals which are their own defence systems and can act as herbicides. Selected examples of guaianolides and heliannuols, which are sesquiterpenes, are discussed in the context of their potential use as natural herbicide templates.

Keywords: Allelopathy; sesquiterpene; herbicide; bioassay; standard target species

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1 INTRODUCTION
The indiscriminate use of herbicides has provoked an increasing incidence of resistance in weeds and new, more efficient and specific herbicides are needed.

Plants and micro-organisms contain allelochemicals which act as their defence system and may act as herbicides. Thus naturally occurring allelochemicals may act as templates for the synthesis of active compounds for use as herbicides[1–5] There have been several reports of the action of sesquiterpene lactones, which occur as allelochemicals in some plants, as inhibitors of plant germination and growth.[6,7] This activity has been attributed to analogues of compounds containing a methylene-γ-lactone moiety. We have isolated such compounds from the leaves of sunflowers (*Helianthus annuus* L)[8,9] and have synthesised a number of guaianolide, eudesmanolide, germacranolide, *cis,cis*-germacranolide, heliangolide and melampolide analogues.[10] As part of an on-going search for new agrochemicals based on allelopathic properties, we have synthesised some guaianolides and heliannuols based on those present as biocommunicators in selected sunflower cultivars and tested them for their ability to affect germination and root and shoot growth of some test plants.

2 EXPERIMENTAL
2.1 Compounds
Figure 1 shows a selection of sesquiterpene lactones isolated from natural sources and/or synthesised from the readily available compound dehydrocostuslactone.

2.2 Seed germination and root and shoot growth bioassays
Stock test solutions in water (10^{-3} M) of pure test compound, or of the commercial herbicide mixture terbutryn + triasulfuron (Logran, Novartis), were diluted to the appropriate concentration and adjusted to pH 6.0, using 2-(*N*-morpholino)ethanesulfonic acid. The test solution (5 ml), or a water control, was added to a sheet of filter paper contained in a Petri dish, seeds of the appropriate test plant were added and the dish was then incubated in the dark in a growth chamber at 25 °C. The test species were as follows (number of seeds and incubation time in parentheses): lettuce, *Lactuca sativa* L cvs Nigra and Roman (25; five days); tomato, *Lycopersicon esculentum* L (25; five days); onion, *Allium cepa* L (25; five days); cress, *Lepidum sativum* L (25; three days); barley, *Hordeum vulgare* L (10; five days) and wheat, *Triticum aestivum* L (10; five days). There were four replicate dishes per treatment, except for wheat and barley, which had 20 replicates. A similar number of controls incorporating seeds incubated on filter paper treated with water was included. The extent of germination, root and shoot length were recorded and subjected to Welch's test which determines differences, significant at $P = 0.01$, between the treatment and the control.